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# CATALYSIS OF HYDRIDE TRANSFER IN STRONG ACIDS

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ABSTRACT - (A) Adamantane and several of its derivates have been found to catalyze intermolecular hydride transfer reactions. They function under a range of conditions from aprotic solutions of aluminum bromide in methyl-bromide to sulfuric acid.

## (A) Catalysis of the Intermolecular Hydride Transfer Reaction by Adamantane

The intermolecular hydride transfer reaction is a characteristic reaction of carbonium ions and alkanes in strong acids. Tertiary alkyl cations take part in the reaction in acids at least as strong as 85-90 percent sulfuric acid[1]. This process is most likely the rate determining step in the carbonium ion chain reaction of isobutane with olefins (commercial alkylations) and is an important element of many alkane isomerization reactions[2].

Because of its importance in the conversion of alkanes, it is natural to consider means of accelerating or catalyzing the reaction. One approach lies in the question of which media provide the most reactive carbonium ions. Another would be to search for a reagent which was a specific catalyst for the reaction. In developing the first approach a solution to the latter was unexpectedly encountered. This was that adamantane has the ability to catalyze the intermolecular hydride transfer reaction. How it was found and a hypothesis regarding its behavior is one of the subjects of this paper.

The hydride transfer reaction was studied in some detail by Bartlett, Condon and Schneider in the 40's who found that t-alkyl halides would rapidly react with potential hydride donors when they were contacted with solutions of aluminum bromide. The reactions were best understood by assuming that the alkyl halide ionized to form a reactive carbonium ion which converted to an alkane in a rapid bimolecular reaction with a t-hydride donor[3].

Further information regarding the dynamics of the process were afforded by NMR observations of isobutane reacting with low levels of the t-butyl cation in solutions of aluminum bromide in 1,2,4 trichlorobenzene[4,5]. Solutions prepared with water as a promoter exhibited partially collapsed signals ($^1$H) for the methyl groups and for the methine hydrogen which did not change noticeably over a 40° temperature range. This led to an estimate of an activation energy barrier of less than one kcal/mol for this hydride transfer reaction. Later NMR studies by Hogeveen and Gaasbeek indicated that the reaction between sec-ions and donors (the isopropyl cation and propane) in $SbF_5$ solutions had just a slightly higher barrier[6a].

The vapor phase hydride transfer reaction has been extensively studied[7]. Both equilibria and kinetic studies have been made, mainly for reactions of t-cations with isoparaffins. Under mass spectrometer conditions the energy barrier has also been found to be very low. For these reactions the activation enthalpy is generally thought to be close to zero. The reaction appears to be entropy controlled and was usually found to slow down as the temperature was raised.

There appears to be a dearth of information regarding the temperature dependence of the hydride transfer reaction under homogeneous conditions in sulfuric acid or hydrofluoric acid. Mechanistic studies, however, clearly indicate that the process occurs more rapidly than deep seated ionic rearrangements (methylpentyl → dimethylbutyl) but slower than the ions undergo

reversible proton exchange and simple 1,2 hydride and alkyl shifts in these solutions. The activation energies for the conversion of 3-methylpentane to 2-methylpentane and 2,3-dimethylpentane to 2,4-dimethylpentane under heterogeneous conditions in sulfuric acid have been found to be 6.4 and 4.9 kcal/mol, respectively, but relating these values to the hydride transfer step per se has been questioned because of concerns about concomittant catalyst degradation during the experiments[8]. Such changes would have the natural effect of altering the concentrations of the carbonium ions and make the interpretation of rate differences difficult.

Also unknown are the concentrations of the alkyl ions and the specific rate constant for the hydride transfer reaction in acids at the low end of the superacid scale (conc. sulfuric acid). The major reason for this is the lack of a suitable probe to measure the concentration of the ions. Perhaps $^{13}C$ NMR could be used but it has not been employed. $^{1}H$ NMR is unsuitable because of rapid exchange processes which average the ions signals with those of the acid.

Because of the absence of this data, it is not possible to compare the inherent reactivity of ions in these systems which are widely employed, with that observed in a number of stronger acid systems that have the ability to stabilize ions so that they are amenable to study by NMR. In the latter acids the energetics of many ionic rearrangements and of many inter- and intra-molecular hydride transfer reactions have been studied extensively[6b].

## DISCUSSION

Adamantane was found to be an effective hydride transfer catalyst while being used to assess the ability of strong acid systems to solvate carbonium ions. Because the 1-adamantyl ion is a bridgehead species, its interaction with any solvating solution must be predominantly with nucleophiles located on one side of its vacant p-orbital, i.e., suprafacially. By contrast most alkyl cations are planar and their vacant p-orbital may interact with nucleophiles situated on both sides of the plane.

Thus one a priori expects alkyl ions to be more strongly solvated than the adamantyl ion in any nucleophilic medium. The relative strengths of solvation may be probed by measuring the position of equilibria which reflect this factor. A convenient measure is the position of a hydride transfer equilibrium in solution relative to that observed in the gas phase. Thus in the reaction of a t-butyl cation with adamantane to yield isobutane and the adamantyl ion, one has an equilibrium involving a pair of cations which ought to differ widely in their interactions with solvating media. By comparing the gas phase equilibrium which favors the formation of the adamantyl ion and isobutane by 4 kcal/mol with estimates of the likely equilibrium in strongly solvating solutions (from relative rates of solvolyses of the bromides) of about 4.5 kcal/mol in the other direction, it may be deduced that this hydride transfer equilibrium should span a range of about 8.5 kcal[9].

While measuring equilibria, it was noticed that the 1/2 width of the $^{1}H$ NMR band reflecting an averaged signal for the methyl protons of isobutane and the t-butyl cation was narrowed markedly when adamantane was added to the t-butyl ion. This may be seen by observing Figs. 1 and 2 which exhibit mixtures of the t-butyl ion with adamantane and norbornane. The position of the butyl signal is different in these samples because the equilibria are quite different. What is more important for the present discussion is that the halfwidth is about 4.3 Hz in the solution containing adamantane and more than 40 Hz in the mixture with norbornane.

The spectrum of Fig. 1 also contains a sharp singlet for the averaged $CH_2$ signals of adamantane and the adamantyl ion and a small, broad band which averages the methine hydrogens of adamantane, isobutane and the adamantyl ion. Spectral integration accounts for all the components of the mixture and the spectrum is generated by adding adamantane to a solution of the t-butyl ion or isobutane to a solution of the adamantyl ion. Hence, Fig. 1 can be understood as depicting the existence of a rapid reversible hydride transfer reaction.

The spectrum of Fig. 2 shows a much broader singlet for the methyl groups of the butyl system under similar experimental conditions. The spectrum also shows distinct resonances for the norbornyl cation and norbornane. This means that hydride transfer reactions between norbornane

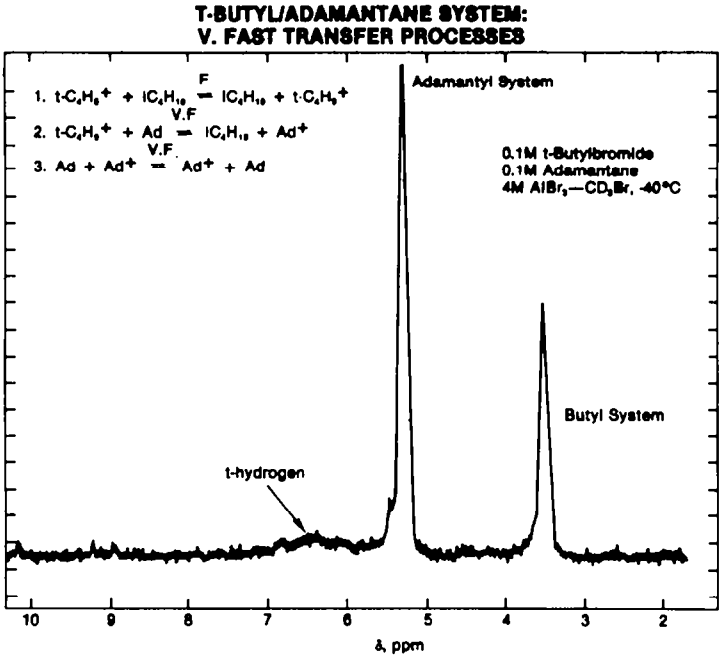
T-BUTYL/ADAMANTANE SYSTEM:
V. FAST TRANSFER PROCESSES
1. t-C4H9+ + IC4H10 F IC4H10 + t-C4H9+
2. t-C4H9+ + Ad V.F IC4H10 + Ad+
3. Ad + Ad+ V.F Ad+ + Ad
Adamantyl System
0.1M t-Butylbromide
0.1M Adamantane
4M AlBr3—CD3Br, -40°C
Butyl System
t-hydrogen
10 9 8 7 6 5 4 3 2
δ, ppm

FIG. 1

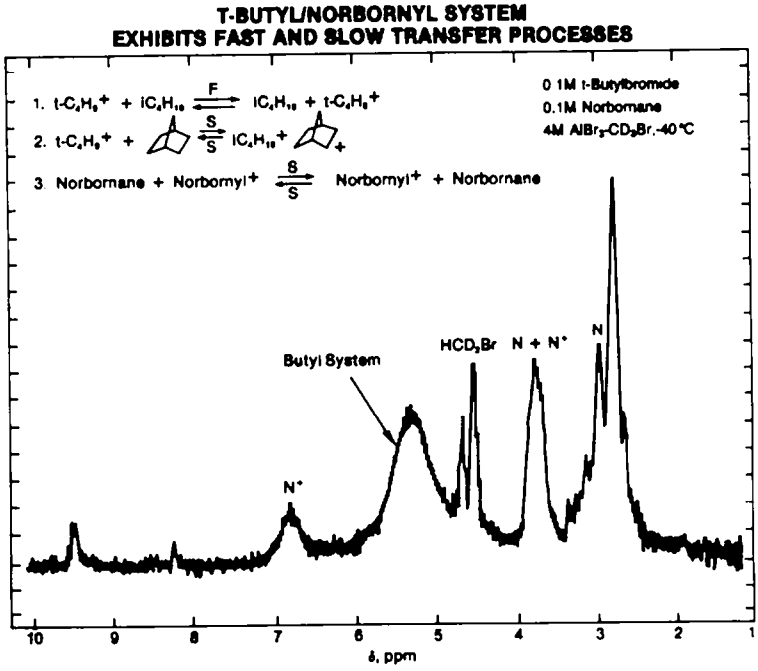
T-BUTYL/NORBORNYL SYSTEM
EXHIBITS FAST AND SLOW TRANSFER PROCESSES
1. t-C4H9+ + IC4H10 F IC4H10 + t-C4H9+
2. t-C4H9+ + S S IC4H10+
3. Norbornane + Norbornyl+ S S Norbornyl+ + Norbornane
0.1M t-Butylbromide
0.1M Norbornane
4M AlBr3-CD3Br, -40°C
Butyl System
HCD2Br
N + N*
N
N*
10 9 8 7 6 5 4 3 2 1
δ, ppm

FIG. 2

and either the t-butyl ion or the norbornyl cation are relatively slow and that the broad butyl band essentially reflects the rate of reaction between isobutane and the t-butyl ion alone.

The marked difference in halfwidth of the butyl signal in these samples is indicative of a strong catalytic effect on the hydride transfer reaction due to adamantane. This effect can be rationalized by considering the likely nature of the transition state for this reaction. Thus the usual reaction between a tertiary cation and a branched alkane probably involves an essentially linear configuration, i.e., the receiving C atom being in line with the breaking C-H bond, because of large steric interactions between the remote groups on the reactants. That these nonbonded interactions must be large can be deduced by examining molecular models of representative systems (such as isobutane-t-butyl ion). From the models it is apparent that the alkyl groups on each of the components approach one another more closely than do the geminal methyl groups on the isobutane molecule. Since it is known that there is a substantial barrier to internal methyl rotation in isobutane (ca. 4.7 kcal)[10], it is clear that there will be a much larger barrier to an internal rotation of one butyl group relative to the other in this transition state.

As a result of this barrier, the normal hydride transfer transition state can be considered to be frozen with respect to this motion. By contrast, the transition state involving adamantane and a t-butyl ion would be expected to have practically no steric barrier to the analogous rotation and the molecular complex ought to approach the behavior of a free rotor.

The presence of a free rotation in one case and not in the other is expected by rate theory to lead to a difference in preexponential factors of about an order of magnitude[11,12] (that with the rotation being larger) and this provides a convenient rationalization of the NMR results.

The proposed explanation implies that adamantane should function as a general hydride transfer catalyst and not be limited to the system in which it was first detected. This thesis has been tested by examining the effect of the reagent upon a reaction whose rate is believed to be limited by the hydride transfer process.

For an initial trial the isomerization of 3-methylpentane to 2-methylpentane in sulfuric acid was chosen as a model reaction. The reaction was studied under heterogeneous conditions with sulfuric acid as the catalyst and found to be accelerated upon the addition of adamantane to the system. The relative isomerization rates are shown in Table 1. This is a simple reaction, generally believed to be occurring via a carbonium ion chain mechanism wherein 3-methylpentane transfers a hydride ion to a cation in the acid, thus forming a new cation which can isomerize and a product molecule[2a,8]. The conversion of 3-methylpentane to its isomer occurs in sulfuric acid without the formation of dimethylhexanes or n-hexane.

The results show that the isomerization is catalyzed by adamantane. Thus increasing its concentration in the substrate to 0.1 and 0.3M led to an increase in the relative rate of isomerization by 56 and 164 percent. Carbonium ion reactions under heterogeneous conditions in sulfuric acid have been shown to proceed both in the acid phase and in the interfacial region[1]. This complicates a kinetic interpretation of the present data, but suggests a further test of the adamantyl moiety as a hydride transfer catalyst. In particular, it ought to be possible to accelerate the 3-methylpentane isomerization in sulfuric acid by employing a surfactant containing the adamantyl group. Such a result would lend further support to both the efficiency of the reagent and the importance of interfacial hydride transfer reactions in this acid.

The investigation of this subject was conducted by establishing that 4-1'adamantylbutylamine behaved like a normal surfactant in sulfuric acid and then employing it as a catalyst for the methylpentane isomerization. Figure 3 shows the surface tension of the acid (as determined with a ring balance) as a function of reagent concentration. Also shown are the relative rates of isomerization. It is clear that there is a close correspondence between the concentration at which the adamantyl surfactant begins to lower the surface tension and where it acts as a catalyst.

The efficiency of 4-1'adamantylbutylamine as a catalyst is compared with that of less surface active derivatives in Table 2. 1-Aminoadamantane and the methyl, ethyl and propyl homologues are

TABLE 1

Adamantane Catalyzes 3-Methylpentane Isomerization[a] in $H_2SO_4$

Overall Reaction: $3MC_5 \rightarrow 2MC_5$

Rate Determining Step: $3MC_5 + 2MC_5^+ \rightarrow 2MC_5 + 3MC_5^+$

| $[Adamantane]_{3MC_5}$, M | $k \times 10^6$, $s^{-1}$ |
|---|---|
| 0 | 3.08 |
| 0.1 | 4.80 |
| 0.3 | 8.15 |

(a) The reactions were carried out at ambient temperatures in a 300 ml, magnetically stirred, stainless steel reactor using equal volumes of 3-methylpentane and conc. sulfuric acid, 95.9%.

Table 2

Isomerization of 3-Methylpentane Catalyzed by Adamantyl Derivatives in $H_2SO_4$

| Additive | Conc., M x $10^3$ | k, $hr^{-1}$ |
|---|---|---|
| None | | 0.017 |
| 1-Adamantyl-X | | |
| $-NH_2$ | 5 | 0.017 |
| $-CH_2NH_2$ | 5 | 0.017 |
| $-CH_2CH_2NH_2$ | 5 | 0.017 |
| $-CH_2CH_2CH_2NH_2$ | 5 | 0.031 |
| $-CH_2CH_2CH_2CH_2NH_2$ | 5 | 0.095 |
| $-CH_2CH_2CH_2CH_2NH_2$ | 2 | 0.050 |
| $-[CH_2]_3$ COOH | 2 | 0.059 |
| $-[CH_2]_4$ COOH | 2 | 0.066 |
| $-[CH_2]_5$ COOH | 2 | 0.121 |

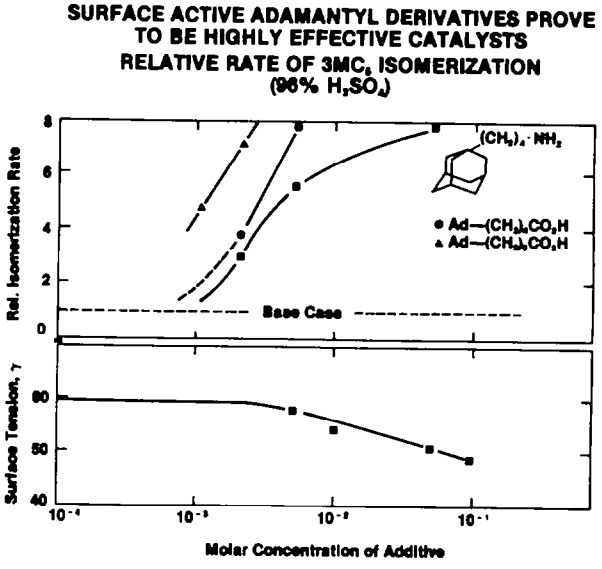


FIG. 3

not nearly as useful as catalysts for the reaction. This is primarily attributed to their being poorer surfactants rather than the existence of a destabilizing electrostatic interaction between the ammonium ion on the tail of the shorter molecules and development of a second cationic charge on the molecule in the hydride transfer transition state.

Also shown in Figure 3 is the effect of replacing the amino group with a carboxylic function. 4-1'Adamantylbutanoic acid (not shown) functions about as well as 4-1'adamantylbutylamine and the longer chain pentanoic and hexanoic derivatives are still more active. The isomerization results, therefore, buttress prior conclusions about the location of the hydride transfer site in sulfuric acid and show that adamantane is a general catalyst for the reaction, being able to function in strongly protic media as well as in aprotic super acid solutions such as those containing aluminum bromide.

## EXPERIMENTAL

NMR measurements were made with 4M $AlBr_3$ solutions in $CD_3Br$ following procedures used previously[9]. The $AlBr_3$ was prepared by sublimation and stored in a nitrogen "Dry Box" until it was used. Stohler's 99.5% D methyl bromide was used as received. A typical solution was prepared in the anhydrous atmosphere by weighing 0.534g of $AlBr_3$ into an NMR tube. The tube was cooled to -80°C and 0.5 ml $CD_3Br$ was distilled into it through a small drying tube containing $CaCl_2$. The acid was dissolved by shaking for about 10 seconds, the solution cooled again, and t-butylbromide added by a syringe to provide an 0.1M solution. The solution was shaken for another second and kept at -50°C until its spectra was obtained at -40°C on a Varian 360-L NMR spectrometer.

The catalysis of the isomerization of 3-methylpentane by adamantane was conducted in a 2-neck 500 ml glass flask immersed in a water bath at 24 +/- 1 'C. The flask contained 100 ml of reagent grade 96% H2SO4 and 100 ml of 3-methylpentane solutions. It was stirred vigorously and sampled periodically throughout a 24 hour period. The products were analyzed by gas chromatography and rate constants obtained from 1st order plots, (Table 1).

Isomerization with adamantylalkylamines was done in a 300 ml magnetically stirred autoclave at ambient temperatures. The experiments used 50 ml of 3-methylpentane and 50 ml of sulfuric acid solutions (prepared with a new supply of acid) containing the amines at concentrations varying from 0.001 to 0.05M, (Fig. 3 and Table 2).

4- '1 Adamantylbutylamine and the analogous propyl and ethylamines were used as obtained from the Aldrich Chemical Company. They were synthesized by Dr. S. Branca following the general procedures established by Fieser, L. F., Nazer, M.Z., Berberian, D.A. and Slighter, R.G., J. Med. Chem. (1967), 10, 517. Adamantylamine and adamantylmethylamine were also purchased from Aldrich.

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